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(19)

(54) REMOVAL OF METALLIC CONTAMINANTS FROM BITUMINOUS MATERIALS

(71) We, COAL INDUSTRY (PATENTS) LIMITED, a company organised in accordance with the laws of Great Britain, of Hobart House, Grosvenor Place, London, S.W.1X 7AE England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed. to be particularly described in and by the following statement:—

This invention relates to the removal of metallic contaminants from bituminous materials, and relates, in particular but not exclusively, to the removal of zinc contaminants from tars and pitches.

In the operation of a coke oven, coal is heated in the oven to drive off the volatile content thereof and leave coke, which contains substantially only carbon and ash. The volatile content of the coal is distilled off and collected. It forms into three fractions, these being a tar fraction, a liquor fraction and coal gas. The liquor is usually ammoniacal. The tar may be further refined by distillation to give pitches as residues, which may find use as binders for the manufacture of carbon electrodes, particularly for electrodes to be used in aluminium smelting plants. Such aluminium grade electrodes must be relatively free of metals, especially zinc and vanadium, and therefore all the constituents of the electrode, including the binder pitch, must also be relatively free of these metals.

Most coals, and some more than others, contain zinc and vanadium, and during the coking, it is possible for these metals to be distilled over into the tar in the form of volatile compounds or complexes. In the case of zinc the distillable material may be either zinc chloride or a complex of zinc with ammonia. These metals tend to be retained in both the tar and the pitches, thus reducing their value as binders for aluminium grade electrodes. Typically a tar may contain from 0.015 to 0.03% of zinc. This tar, on distillation will give rise to pitches containing about 0.04% zinc, which is well in excess of the 0.01% deemed the upper limit for binder pitches.

It is therefore desirable that some if not all of the metallic contaminent should be removed from the tar or pitch fractions. It has been proposed to achieve this by centrifugation of the pitch or tar at a temperature at which the pitch or tar is not too viscous. However this method, although fairly effective in removing the zinc and other metals in the form of solid compounds also removes certain components of the tar or pitch which are solid at the temperature of centrifuging. These components are insoluble in toluene and partly insoluble in quinoline. These components form a good basis around which the pitch or tar may be carbonised to form coke. Therefore the binding properties of the tar or pitch for use in electrodes are adversely affected by the removal of these toluene and quinolene insoluble materials.

It is therefore an aim of the present invention to provide a method of reducing the content of metallic contaminants in tars and pitches without substantially removing any useful component of the tars and pitches.

Therefore according to the present invention there is provided a method of reducing the content of a metallic contaminant in a bituminous material comprising forming, at a temperature at which the bituminous material is liquid, a dispersion of the bituminous material and a solution containing a complexing agent for the metallic contaminant, wherein either one of the components of the dispersion forms a continuous phase, maintaining the dispersion for a sufficient time so that the complexing agent forms, with a substantial portion of the metallic contaminant, a complex soluble in the solution, and separating the bituminous material from the solution.

The dispersion of the present invention either may be a true emulsion, in that the disperse and continuous phases are maintained by chemical forces, or may be a mechanically-maintained dispersion. In the latter case the dispersion is maintained by mechanical agitation in a suitable machine, for instance a blade mixer.

The dispersion may be originally formed either by feeding liquid bituminous material and the solution in the suitable machine, or by spraying the bituminous material into the solution. It is preferred that the dispersion is not a true emulsion, since to separate the bituminous material from the solution, it will be necessary to include in the method of the invention a step in which the emulsion is broken. This will add to the cost of carrying out the method of the invention. Nonetheless, mixing to form an emulsion is within the scope of the invention.

The separation may be effected either by settling, if there is no emulsion present, or by chemical separation and settling if an emulsion is present. However, in either the presence or absence of an emulsion, the preferred method of separation is by centrifugation, particularly in a continuous centrifuge.

It is preferred that approximately equal volumes of bituminous material and solution should be mixed, although the ratio of the volumes may vary from 100 to 1 of bituminous material to 10 of solution.

Since a dispersion must be formed, the bituminous material and the solution must be substantially immiscible. Therefore only polar solvents, preferably water, will be usable as the solvent in the method of the invention.

The complexing agent may be selected so that it removes predominantly only one metal, or may be relatively non-selective. For example, the complexing agent may be an alkaline agent such as a di- or tri- amine, for instance ethylene diamine, or an alkaline hydroxide, for instance sodium or potassium hydroxide or ammonia.

Since most bituminous materials become liquid below 80°C it is desirable that the method should be carried out at a temperature not above 80°C, especially since at high temperatures there is a possibility that the complexing agent may be driven out of solution or may be destroyed.

It is envisaged that the method of the invention will be embodied in a continuous process in which it will be possible, although not necessary, to recycle both the bituminous material and the solution. If the solution is recycled it may be necessary to have a separation stage for removing the metallic contaminant therefrom, and a make-up stream of complexing agent.

The amount of complexing agent in the solution will vary depending on the metallic contaminant in the bituminous material and on the complexing power of the complexing agent. These amounts however will be easily determinable by the skilled worker.

If the bituminous material is a tar derived from a coke oven a preferred complexing agent for removing zinc is ammonia. This makes it possible to use the coke oven liquor as the solution. It may be necessary to fortify the liquor with ammonia to enable efficient extraction to take place. Preferably, the liquor or solution contains from 15-20% by weight of ammonia. If sodium or potassium hydroxide is used, it is possible to use less concentrated solutions, suitably from 1 to 10%, preferably approximately 2.5%, by weight.

One application of the present invention will now be described by way of example only, with reference to the formation of a pitch binder for aluminium grade electrodes.

EXAMPLE

A batch of bituminous coal (CRC 301, according to "The Coal Classification System used by the National Coal Board." 1964), which has a zinc content of 0.004%, is coked in a conventional coke oven battery. The distillate which comprises an ammoniacal liquor and a tar is removed. The tar contains from 0.02 to 0.03% of zinc, either in the form of zinc chloride or as a solid ammoniacal complex. If this is further fractionated to give a pitch having a softening point suitable for use as an electrode binder the pitch has a zinc content of approximately 0.04% by weight, which is too high for it to be used as a binder pitch. Therefore the tar and liquor are made to equal volumes and the liquor is fortified with ammonia to make the ammonia content approximately 17% by weight. The tar and liquor are mixed in a blade mixer at a slow mixing speed for 60 min. The mixture is fed to a continuously operating centrifuge which separates the liquor from the tar. The zinc content of the tar is reduced to about 0.005%, and the pitch which can be separated therefrom contains less than 0.01% by weight of zinc, and can therefore be used as a binder for aluminium grade carbon electrodes.

WHAT WE CLAIM IS:—

1. A method of reducing the content of a metallic contaminant in a bituminous material comprising forming, at a temperature at which the bituminous material is liquid, a dispersion of the bituminous material and a solution containing a complexing agent for the metallic contaminant, wherein either one of the components of the dispersion forms a continuous phase, maintaining the dispersion for a sufficient time so that the complexing agent forms, with a substantial portion of the metallic contaminant, a complex soluble in the solution, and sepa-

rating the bituminous material from the solution.

2. A method according to claim 1, wherein the bituminous material is a coal tar pitch.

3. A method according to claim 1 or 2, wherein the dispersion is a mechanically maintained emulsion.

4. A method according to claim 1, 2 or 3, wherein the separation is effected by centrifugation.

5. A method according to any one of the preceding claims, wherein the bituminous material is present in the dispersion in a volume ratio of 100 to 1:10 of the solution.

6. A method according to claim 5, wherein the volume ratio is approximately 1:1.

7. A method according to any one of the preceding claims, wherein the solvent of the solution is water.

8. A method according to claim 7, wherein the complexing agent is an alkaline hydroxide.

9. A method according to claim 7, wherein the complexing agent is a di- or triamine complexing agent.

10. A method according to claim 8, wherein the complexing agent is ammonia.

11. A method according to claim 8, wherein the complexing agent is sodium or potassium hydroxide.

12. A method according to claim 1, substantially as hereinbefore described with reference to the Example.

13. A bituminous material having a reduced content of metallic contaminant, whenever produced by a method according to any one of the preceding claims.

14. A pitch produced from a coal tar which has a reduced content of metallic contaminant, produced by a method according to any one of claims 1 to 12.

For the Applicants,
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